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Analysis of migration of polyfluorinated compounds from paper packaging into food matrices

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Introduction. Polyfluorinated compounds are extensively utilized as grease- and water repellants in paper- and cardboard used as food contact materials. These bioaccumulative substances are able to migrate from the food contact material into foods. In this study, we compare two extraction methods for polyfluorinated compounds in food samples; liquid-liquid extraction by trifluoroethanol and methanol extraction/saponification/weak ion exchange solid phase clean-up.

Materials and methods.

Two food products; popcorn and flour, were extracted with LLE [1]] and with SPE [2].Extraction scheme for the SPE method is presented in Figure 1. LLE was performed by a two-phase system where 0.2 g food product were extracted by 5 mL of isooctane and 2 mL 80:20 (v:v) trifluoroethanol and water. Products were simulated for storage and usage and pre-treated according to Table 1.

The compounds analysed were polyfluorinated mono- an di-alkyl phosphate esters (monoPAPs, diPAPs, and S-diPAPs). The analysis was performed by HPLC-MS-MS for the SPE method or by UHPLC-MS-MS for the LLE technique. C_{13}-labelled standards was used as internal standards.

Table 1. Pre-analysis treatment of food products and food simulants.
* Saponfication step only for SPE.

Food product	Storage simulation	Usage simulation	Pre-treatment
Popcorn	NA	Popped	Cryohomogenised, saponificated*
Fluor	40 °C, 10 days	NA	Saponificated*

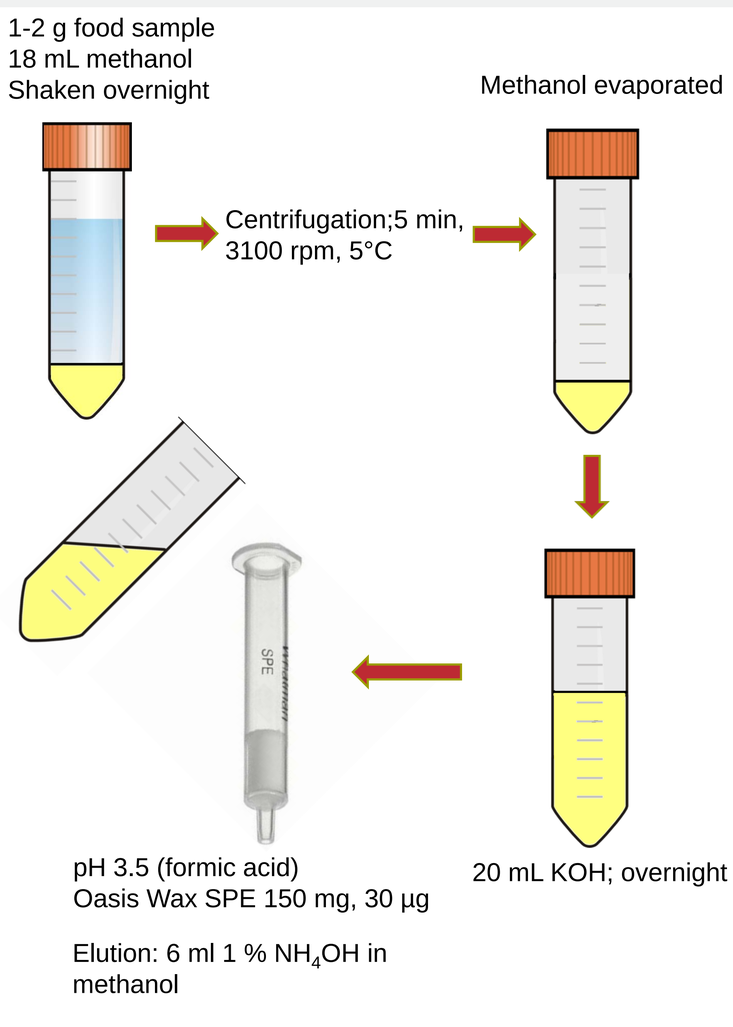

Figure 1. Extraction scheme for the methanol extraction/saponification/weak ion exchange solid phase clean-up. The SPE clean-up were performed according to the manufacturer's protocol

Compound/ Sample	4:2 mono-PAPs	6:2 mono-PAPs	8:2 mono-PAPs	10:2 mono-PAPs	4:2/4:2 di-PAP	6:2/6:2 di-PAP	8:2/8:2 di-PAP	10:2/10:2 di-PAP
Popcorn 1	0	120	110	106	5	106	120	115
Popcorn 2	0	96	82	63	4	127	94	78
Popcorn 3	0	120	118	141	6	123	134	122
Popcorn 4	0	103	104	122	5	108	112	98
Mean revovery (%)	0	110	104	108	5	116	115	103
Relative std (%)	-	9	13	26	10	8	12	16

Table 2. Mean recovery and relative standard deviation for spiked popcorn (500 ng/g) extracted by the LLE method.

Compound/ Sample	4:2 mono-PAPs	6:2 mono-PAPs	8:2 mono-PAPs	10:2 mono-PAPs	4:2 di-PAPs	6:2 di-PAPs	8:2 di-PAPs	10:2 di-PAPs
Fluor 1	0	132	105	180	5	106	106	261
Fluor 2	0	127	100	113	4,	119	94	254
Fluor 3	0	105	92	123	5	100	103	139
Fluor 4	0	124	121	189	5	110	118	184
Mean revovery (%)	0	122	104	151	5	109	105	209
Relative std (%)	-	8	10	22	4	6	8	24

Table 3. Mean recovery and relative standard deviation for spiked flour (500 ng/g) extracted by the LLE method.

Compound/ Sample	4:2 mono-PAP	6:2 mono-PAP	8:2 mono-PAP	10:2 mono-PAP	4:2/4:2 di-PAP	6:2/6:2 di-PAP	8:2/8:2 di-PAP	10:2/10:2 di-PAP
42 ng/g	73	59	102	12	100	70	246	64
88 ng/g	58	51	95	11	9	43	151	51
570 ng/g	64	53	107	2	91	55	223	37
Mean recovery (%)	65	54	101	8	67	56	207	51
Relative std (%)	9	6	5	54	61	20	20	22

Table 4. Mean recovery and relative standard deviation for spiked popcorn extracted by the SPE method. n=3 for each level of spiking.

Compound/ Sample	4:2 mono-PAPs	6:2 mono-PAPs	8:2 mono-PAPs	10:2 mono-PAPs	4:2/4:2 di-PAPs	6:2/6:2 di-PAPs	8:2/8:2 di-PAPs	10:2/10:2 di-PAPs
20 ng/g	20	96	7	58	26	73	275	435
94 ng/g	11	253	35	59	18	105	360	789
Mean recovery (%)	16	175	21	58	22	89	317	609
Relative std (%)	29	45	67	1	18	18	13	29

Table 5. Mean recovery and relative standard deviation for spiked flour extracted by the SPE method. n=3 for each level of spiking.

Results and Discussion

Since 2010, it is recommended by the European Council, to monitor mono- and di-PAPs in food products. We have compared the two most common extraction strategies for per- and polyfluorinated compounds used for food products.

Test for the extraction efficiency of migrated flourinated compounds into food products:

- The trifluoroethanol extraction method revealed high recovery for for mono-PAPs and di-PAPs. This method included internal standards of 6:2 mono-PAPs, 8:2 mono-PAPs, 6:2 di-PAPs and 8:2 di-PAPs. The recoveries of 4:2 monoPAPs and 4:2/4:2 diPAPs are insufficient, probably due to degradation of these compounds in the non-commercial standard. All other standards used were commercially obtained.

- On the contrary the SPE method only included 6:2 di-PAPs as internal standard. The recovery was fair for the 6:2 di-PAPs but it is evident that the accuracy is not adequate for some of the other compounds. However, omitting the internal standard resulted in too low recoveries. Including more internal standards is essential for better accuracy and precision. Therefore, further analysis is necessary to validate this method.

Conclusion

The liquid-liquid extraction provides a simple, and efficient, method for the extraction of mono- and diPAPs in food matrices relevant for surveying potential migrating polyfluorinated compounds from food contact materials. The SPE method, which have good recoveries for PFCs (data not shown), had relatively poor accuracy. This study further emphasizes the necessity for using compound specific internal standards, preferable for each analyte.

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